NATIONAL BUREAU OF STANDARDS REPORT

10 422

Progress Report

on

DETERMINATION OF THE DEGREE OF POLYMERIZATION OF A POLYMERIC AROMATIC AMINE FROM NMR DATA USING A "LEAST-SQUARES" APPROACH

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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> Office of Standard Reference Data—Clearinghouse for Federal Scientific and Technical Information [3]—Office of Technical Information and Publications—Library—Office of Public Information—Office of International Relations.

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.
[2] Located at Boulder, Colorado 80302.
[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

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DETERMINATION OF THE DEGREE OF POLYMERIZATION OF A POLYMERIC AROMATIC AMINE FROM NMR DATA USING A "LEAST-SQUARES" APPROACH

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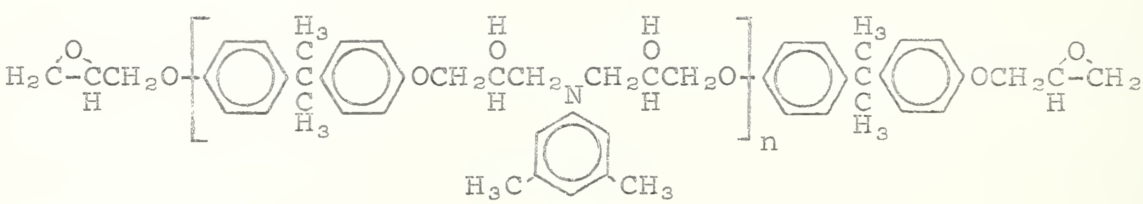
Synopsis

A polymeric amine, the reaction product of 3,5-xylidine and the diglycidyl ether of bisphenol A, which had been synthesized and reported elsewhere, was analyzed by nuclear magnetic resonance spectroscopy (NMR). A statistical method was derived to estimate the degree of polymerization based on linear multiple regression analysis of the intensity of the NMR absorption peaks.

DETERMINATION OF THE DEGREE OF POLYMERIZATION OF A POLYMERIC AMINE FROM NMR DATA USING A "LEAST-SQUARES" APPROACH

In a previously submitted paper[1] a method of using nuclear magnetic resonance (NMR) data for the determination of <u>n</u> for the polymeric amine (the reaction product of 3,5-xylidine and the diglycidyl ether of bisphenol A) shown was presented. In that paper, <u>n</u> equalled 1/(R-1) where R, the molar ratio of bisphenol A segment to 3,5-xylidine segment, was determined by linear regression of the mean intensities of the various peaks on the mean intensity of the benzylic peak (adjusted to reflect the number of protons in each of the two segments responsible for each peak) assuming no experimental error in the latter and zero intercept.



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An alternative and more general procedure for determining $\underline{n}$ is as follows:

Since the intensity of a given NMR peak is assumed to be proportional to the number of protons of a given configuration causing the peak[2] we may set up the following system of simultaneous linear equations:

$$\sqrt{w_1}\, I_{CH_3*} = \sqrt{w_1}\,\underline{k}(6\underline{n} + 6) = 6\sqrt{w_1}\,\underline{nk} + 6\sqrt{w_1}\,\underline{k}$$

$$\sqrt{w_2}\, I_{aromatic} = \sqrt{w_2}\,\underline{k}(11\underline{n} + 8) = 11\sqrt{w_2}\,\underline{nk} + 8\sqrt{w_2}\,\underline{k}$$

$$\sqrt{w_3}\, I_{aliphatic} = \sqrt{w_3}\,\underline{k}(10\underline{n} + 10) = 10\sqrt{w_3}\,\underline{nk} + 10\sqrt{w_3}\,\underline{k}$$

$$\sqrt{w_4}\, I_{CH_3} = 6\sqrt{w_4}\,\underline{nk}$$

where w is a statistical weighting factor inversely proportional to the variance of the intensity of the peak, I is the mean intensity of the peak caused by the protons described by the subscript, CH_3* refers to the methyl groups of the bisphenol segment, CH_3 refers to the benzylic methyl groups (on the xylidine ring), $\underline{k}$ is the proportionality constant relating the intensity of a given peak to the number of protons causing

the peak, and n is the quantity of repeating units in the polymer molecule. (In order to make use of a computer program* for solving unweighted multiple linear regression equations, w_i was chosen in such a way that Σw_i = number of simultaneous equations.)

The experimentally determined values for the intensities (in arbitrary units) of the mean (and standard deviation for a single observation) are I_{CH_3*}, 7.3 (1.5); $I_{aromatic}$, 12.5 (3.4); $I_{aliphatic}$, 13.4 (2.7); and I_{CH_3}, 6.0 (0.40). The weighted standard deviation for a single observation is 0.76. Each value is the result of three determinations.

Using standard techniques,[3] we find that nk equals 1.00 and k equals 0.26. Solving for n, n equals 3.8. The standard error of estimate is 0.205. An F test performed on the ratio of three times the weighted mean square residuals from regression to the weighted variance of the individual observations shows that the error due to regression is consistent with the estimated error of the individual observations

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* A computer program entitled LMREG (copyrighted by Honeywell, Inc, 1970) written in BASIC

at the 95% confidence level, where the factor three puts the mean square residuals in terms of individual intensity values.

The degree of polymerization is defined as the average number of monomer units per polymer molecule.[4] Since the number of amine segments per polymer molecule equals _n_ and the number of bisphenol A segments equals _n_ + 1, the degree of polymerization is 2_n_ + 1 or 8.6 according to the above definition.

Previously, it was implicitly assumed that _nk_ equals 1.00 by correlating all the intensity values with I_{CH_3} which was set equal to 6.[1] If, in the above equations with all weights set equal to 1.0, _nk_ is set equal to 1.00 then _k_ equals 0.269 and _n_ equals 1/_k_ or 3.7 as before.

References

(1) R. L. Bowen and H. Argentar. J. dent. Res., submitted for publication.

(2) L. M. Jackman and S. Sternhall. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd ed," Pergamon Press, Elmsford, N. Y. 1969, p. 13.

(3) M. G. Natrella. "Experimental Statistics," NBS Handbook 91, Washington, D. C. 1963, pp 4-21 and list of errata.

(4) P. J. Flory. "Polymer Chemistry,"Cornell University Press, Ithaca, N. Y. 1953, pp 29-37.

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